THE TECHNICAL NEWS BULLETIN OF THE NATIONAL BUREAU OF STANDARDS / October 1973

DIMENSIONS NBS

ENVIRONMENT:

A Question of Quality

A PUBLICATION OF THE UNITED STATES DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

DIMENSIONS NBS

OCTOBER 1973 / Vol. 57, No. 10 / ISSUED MONTHLY

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Nat. Bur. Stand. (U.S.) DIMENSIONS/NBS
CODEN: NBSTAR 57(10)225–252

Superintendent of Documents Catalog No. C13.13 : 57/10

Library of Congress Catalog No. 25–26527

Man is threatening a natural heritage—the quality of his environment. NBS' contributions to pollution control constitute an essential element of the battle to restore and preserve that heritage. This issue of *DIMENSIONS/NBS* highlights these activities.

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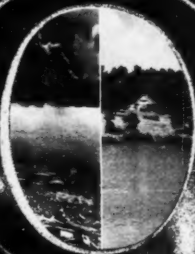
The Institute for Basic Standards
The Institute for Materials Research
The Institute for Applied Technology
The Institute for Computer Sciences and Technology
Center for Radiation Research
Center for Building Technology
Center for Consumer Product Safety

Formerly the TECHNICAL NEWS BULLETIN of the National Bureau of Standards.

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402. Annual subscription: Domestic, $6.50, foreign, $8.25, single copy, 65 cents. The Secretary of Commerce has determined that the publication of this periodical is necessary in the transaction of the public business required by law of this Department. Use of funds for printing this periodical has been approved by the Director of the Office of Management and Budget through June 30, 1976.

MEASURING ENVIRONMENTAL QUALITY



NBS is playing an increasing role in achieving pollution abatement.

THROUGH the Federal Clean Air Act and the Water Pollution Control Act, Congress issued the mandate for protecting our environment from dangerous contamination of our air and water resources. At an estimated cost of $190 billion over the next 10 years the United States is working to attain the levels of air and water quality set by the Environmental Protection Agency (EPA).

The national effort to protect the air and water environments is primarily one of enforcement and control. EPA has the mandate from Congress and the people to protect us from polluted air and water.

The National Bureau of Standards, as a nonregulatory, measurement- and standards-oriented organization, is playing an increasingly important role in assisting the Nation to achieve the goal of pollution abatement. Lacking accurate and generally accepted methods of measurement and reference standards EPA would have difficulty administering its programs. At the same time, industry could not comply economically with the regulations without a firm base of measurement. NBS, working impartially to develop measurement methods and standards, aims to make it possible to protect the public health at minimum economic cost.

The Bureau works in support of the Nation's pollution abatement programs by providing:

- standards for measurement (both standards of methodology and Standard Reference Materials).
- improved measurement techniques and instruments.
- calibration of measurement systems.
- scientific information and data.

Much of the Bureau's work in this area represents a striking example of the coupling of basic research to applied research and engineering.

In mid-August, the Bureau assembled some of its best researchers and measurement experts in a day-long seminar. Assistant Secretary of Commerce for Science and Technology, Dr. Betsy Ancker-Johnson, and NBS Director, Dr. Richard W. Roberts, participated. This issue of DIMENSIONS/NBS describes NBS activities in air and water research in order that the Nation understand the importance of standards work and accurate measurement in improving the quality of our environment.

NBS SHOWS THE WAY TOWARD
CLEAN AIR AND WATER

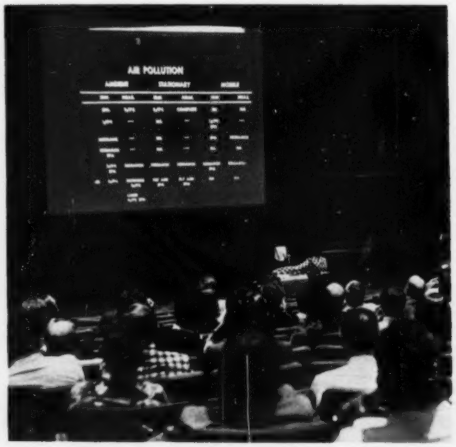
by James R. McNesby, Manager, Measures for Air Quality

THE Clean Air Amendments of December 31, 1970, required that the Administrator of what is now the Environmental Protection Agency set standards for ambient air quality. Six pollutants were designated—carbon monoxide, sulfur dioxide, nitrogen oxides, nonmethane hydrocarbons, photochemical oxidants, and something called particulate matter. To ensure the eventual meeting of the standards for each of the six pollutants in ambient air, control of emissions from stationary sources and from mobile sources (autos) are necessary. For effective implementation of the law, it is required further to ensure the accuracy of the measurements in each element of the pollutant-source matrix.

As Manager of the NBS Measures for Air Quality (MAQ) program since its inception in 1970, it has been my responsibility to see that each element in the matrix receives appropriate attention by staff scientists wherever possible—with EPA funding if available and otherwise with NBS funding. For each measurement area we recognize in general a need for a Standard Reference Material and for research in advanced measurement methodology. We recognize further that, in dealing with the highly reactive gaseous pollutants whose concentrations range from parts per billion to parts per thousand, traditional methods of storage as Standard Reference Materials may be inadequate. Therefore, we envision a need to extend the concept of Standard Reference Materials to unconventional techniques.

In the case of gaseous pollutants we support and encourage such projects as the exponential mixer, critical-flow orifice technology, pyrolytic reactor techniques. EPA supports little measurement research at NBS. Their major support has been in development of Standard Reference Materials where there are short-term needs. The position of the MAQ program office has been to support measurement research when we believe the need exists even though we might be unsuccessful in obtaining funding from the appropriate regulatory agencies. Thus, the particle size analyzer and the sulfur dioxide monitor were developed initially entirely with NBS funding. A prototype of the former is now being built with EPA support, and several American manufacturers are committed to production of the SO_2 fluorescence monitor for stack monitoring.

Other examples in which NBS exerted leadership which later was exploited by other agencies included the early Measures for Air Quality/Office of Standard Reference Data program in air pollutant data evaluation, which spawned the extensive Department of Transportation program in stratospheric pollution, and the examination of the x-ray diffraction signature of Baltimore dust, which earned the attention and eventually the fiscal support of the National Institute for Occupational Safety and Health. This project involved a study of quartz in industrial atmospheres. Again, in the first year of MAQ, a seed project in the Analytical Chemistry Division began the development of the automotive ex-



haust Standard Reference Materials. The next year, the EPA breathed fiscal vitality into this project which will provide the reference gases so important to solution of the automobile exhaust emission measurement problem.

The most difficult auto exhaust Standard Reference Material is NO in nitrogen. This is so important for the evaluation of the 1976 prototype engine which goes on the test stand in November of this year that we are attempting independent verification of the composition of our gases. Included in the following articles is a report on our work on absolute coulometry which is concerned with the measurement of NO. A part of our program is the improvement in the state of the art of auto exhaust measurement. In addition, NBS is working on a novel and fast way to measure NO in auto exhaust and we also have an effort in conjunction with this to measure auto exhaust flow rates with very rapid time resolution.

The Environmental Protection Agency has the responsibility for monitoring radioactivity outside the fence line of nuclear power reactors. The long experience of the scientists in the Center for Radiation Research in ensuring the accuracy of such measurements is obviously relevant to the measurement of radioactivity of air.

We have not such clear-cut measurement tasks delineated by the Federal Water Pollution Control Act of 1972 and in developing our program we will be examining a number of information sources. The EPA and NBS are preparing to enter into a joint project, a tissue bank where long-term trends in trace contaminant content of various tissues can be studied. Our health effects colleagues have been telling us of their priorities in this project and this will help to establish our priorities in measuring the water pollutants that ultimately enter the tissues. Similarly we expect input from those EPA ecologists regarding their priorities in the analysis of the prospective standard river sediment. The EPA water pollution criteria document, now in draft form, contains proposed standards for 81 pesticides, 34 cations, and a number of organics and radioactivity. Also the EPA has a discharge permit program in which discharges of important water pollutants are limited at sources. All of these inputs in addition to our own issue study in IBS on flow measurement provide us with information needed to set our measurement priorities.

INPUTS TO NBS WATER POLLUTION PROGRAM

- EPA/NBS Tissue Bank
- EPA/NBS River Sediment
- EPA Criteria Document
  - 81 Pesticides
  - 34 Cations
  - Organics, Radioactivity
- EPA Discharge Permit Program
- NBS Issue Study on Flow Measurement

The NBS water pollution program will concentrate in FY 74 on the measurement of trace toxic metals in water and in FY 75 our hope is for a much more comprehensive program in the measurement of inorganic and organic pollutants, including pesticides. At present the priorities in the regulatory agencies are shifting and we must maintain a position of flexibility to sieze those opportunities that present themselves as the picture comes more clearly into focus. I believe our air and water programs are coherent, responsible, and imaginative and that we have attracted some of the Bureau's best scientific talent. □

AIR POLLUTION MEASUREMENT MATRIX

	Ambient		Stationary		Mobile	
	SRM	Meas.	SRM	Meas.	SRM	Meas.
SO_2	EPA*	9/73*	9/74	Complete	NA*	NA
CO	1/74		NA		3/74 EPA	——
HC	Methane		NA		EPA	Research*
O_3	Research EPA		NA		NA	NA
NO_x	3/74 EPA	Research	Research	Research	Research EPA	Research
Particulate	6/74	Methods 9/73 Laser 9/73 EPA	Fly Ash EPA	Fly Ash EPA	NA	NA

*EPA: EPA supports
Dates: Completion date
Research: Under investigation at NBS
NA: Not applicable since no regulatory standard has been set by EPA

AIR QUALITY

During 1970, 26 million metric tons of SO_2, 20 million of nitric oxides, 23 million of particulates, 32 million of hydrocarbons, and 134 million of CO_2 were added to the atmosphere in this country alone. Air clean-up efforts cannot be concentrated on just one source: Autos contribute practically no SO_2 but they account for 56 percent of the hydrocarbons.

Accurate measurements are needed to answer such questions as: How much pollution is there now? Where does it come from? Where does it go? Are we making headway in the drive for cleaner air?

WITHOUT accurate measurements of pollutants, enforcement of Clean Air legislation and adherance to levels of clean air set by EPA can at best be expensive and overly restrictive or at worst even unenforceable. Already litigations are arising between industry and government involving the question of the adequacy of measurement technology and practices.

The economic impact of pollution control is difficult to assess. The cost is spread over increased costs of products to consumers, decreased sales of goods, the closing of some plants, increased unemployment, and inflation. However, according to studies reported in the December 1970 issue of the *Journal of the Air Pollution Control Association*, the cost of measuring air pollution is a small fraction of the cost of controlling air pollution. Improvements in measurement techniques can have a magnified effect either on the cost of control or on the cost to the Nation resulting from inadequate control, since the Administrator of EPA is directed to set air quality regulatory levels and control strategies with an "adequate margin of safety." This margin of safety reflects the uncertainty in measurement.

The goal of the NBS Measures for Air Quality program is to provide data, improved measurement techniques, measurement standards, and calibration of measurement systems in support of air pollution abatement programs of other Federal agencies, State and local governments, and industry.

NBS works closely with EPA to help ensure that the technology necessary to enforce and observe the EPA regulations is available. Air quality regulatory levels set by EPA are the products of a comprehensive process to assure:

- that the regulation protects human health and welfare and the environment from harm.
- that the regulation is based on the soundest possible scientific and technical information.
- that the regulation meets all requirements of the law under which it is issued, and that it is legally enforceable.
- that the regulation reflects sound public policy.
- when risks must be balanced against benefits, that the regulation contains a margin of safety on the side of public health and welfare.

A national air quality level sets a limit on the amount of a given pollutant permitted in the air around us. There are two types of air regulatory standards: (1) primary standards—designed to protect public health—set a limit on the amount of a particular pollutant in the ambient air that is safe for humans; (2) secondary standards—designed to protect public welfare—are usually more stringent than a primary standard. They set limits on the amount of a pollutant that is safe for clothes, buildings, metals, vegetation, crops, animals, etc.

Some pollutants are so hazardous that direct controls are placed on their emission into the air. A regulatory emission standard is the maximum amount of that pollutant that may be discharged from a specific source, i.e., smokestacks and automobiles.

The Bureau's program is concerned with three general areas of air measurement: mobile sources, stationary sources, and ambient air. NBS plays a crucial role in furnishing measurement methods of known accuracy, measurement standards for the calibration of pollution-measuring and monitoring instruments, data of importance to scientists and engineers, and information on the mechanisms involved in chemical reactions related to pollution. The main products of MAQ are:

- new techniques for measurement of the concentration of pollutants in air to provide improved sensitivity, accuracy, and reliability over existing techniques and
- Standard Reference Materials for use in the calibration of air pollution monitoring equipment. □

National Primary and Secondary Ambient Air Quality Regulatory Standards

	Primary Standard		Secondary Standard	
	µg/cm³	ppm	µg/cm³	ppm
Sulfur Oxides (Sulfur Dioxide)	80 annual arithmetic mean	0.03	60 annual arithmetic mean	0.02
	365 maximum 24-hour concentration [a]	0.14	260 maximum 24-hour concentration [a,b]	0.10
			1,300 maximum 3-hour concentration [a]	0.5
Carbon Monoxide	10,000 maximum 8-hour concentration [a]	9	same	
	40,000 maximum 1-hour concentration [a]	35	same	
Nitrogen Dioxide [d]	100 annual arithmetic mean	0.05	same	
Hydrocarbons [d]	160 maximum 3-hour concentration (6 to 9 a.m.) [a]	0.24	same	
Particulate Matter	75 annual geometric mean		60 annual geometric mean [c]	
	260 maximum 24-hour concentration [a]		150 maximum 24-hour concentration [a]	
Photochemical Oxidants	160 maximum 1-hour concentration [a]	0.08	same	

Source: Federal Register, April 30, 1971.
[a] Not to be exceeded more than once a year.
[b] As a guide to be used in assessing implementation plans to achieve the annual standard.
[c] As a guide to be used in assessing implementation plans to achieve the 24-hour standard.
[d] The hydrocarbon standard is for use as a guide in devising implementation plans to achieve oxidant standards.

MEASURING
AUTO EMISSIONS

THE automobile is one of the largest contributors to urban air pollution. Three components of automotive exhaust are restricted by EPA regulations: carbon monoxide, hydrocarbons, and nitrogen oxides—all key ingredients in the formation of photochemical smog. Over the next few years more components will be identified and standards set.

NBS work in automotive emissions has taken three approaches: (1) preparation and certification of a series of standard reference gases, (2) development of techniques for the measurement of rapid gas flow, and (3) determination of exhaust emissions of vehicles using different fuels.

STANDARD REFERENCE GASES

The enforcement of automobile emission regulations is seriously limited by the ability of industry and the government to make reliable and reproducible analytical measurements. Uncertainties of 10 to 20 percent are presently reported, due primarily to calibration problems. NBS is currently engaged in a program to provide standard reference gases to serve as primary standards for auto emission measurements.

Two sets of standards are already available from NBS' Standard Reference Materials program[1]—propane in air (SRM's 1665-1669) and carbon dioxide in nitrogen (SRM's 1673-1675). Work on carbon monoxide-nitrogen mixtures is nearing completion while nitric oxide standards are expected to be available yet this fall.

Individual cylinders of each SRM are analyzed by gas chromatography to assure compliance with specifications and to establish a precise relative value for the concentration. The absolute concentration of the gas is determined by relating this precise concentration to the concentration contained in a set of absolute standards. These standards are prepared using a gravimetric technique to measure the weight of both the substance and the air or nitrogen with which it was mixed.

AUTOMOTIVE EXHAUST FLOWRATE MEASUREMENT

Fillmer W. Reugg and James E. Potzick of the Mechanics Division are attempting to develop and evaluate a real-time, essentially nonintrusive, mass rate flow meter for use in measurement of automotive pollutant emissions. A measurement uncertainty of 1 percent is the goal. The objective is to provide a meter that gives a rapid response to changes in the flowrate, that will be external to the exhaust system (to avoid changes in exhaust pressure), that maintains a stable calibration, that will be easily used by a technician in the field, and whose cost is low.

Two approaches have been selected for initial experiments designed to determine the most promising approach. The first involves the use of sonic pulses generated by a spark or other means. The difference in flight time to upstream and downstream pulse sensors is determined. The second approach involves the use of high-frequency (40 kHz) continuous sound waves. The phase difference in these waves at sensors upstream and downstream from the wave source can be measured. Phase difference can be expressed as a time difference.

Both methods can give the mass rate of flow per unit area. Flowrate information in digital form and as a function of the time can be secured with method 1. Method 2 probably cannot follow high-frequency changes in flowrate due to time delays in the electronic apparatus. Some very preliminary tests of method 1 indicate further trials should be made and electronic apparatus is being assembled. Meanwhile other equipment is being assembled for calibration of the sonic and ultrasonic meters under development.

Some consideration was given to the use of a commercial, cooled sensor for mass flow measurement. However, the fouling problem and the difficulty in specifying its performance in rapidly changing gas temperatures made it too unattrac-

tive for investigation at this time, the researchers say.

A commercial ion deflection mass meter has been tested over the density and flow range of interest. Although its performance could be adequate with dry air, its sensitivity to fouling and gas composition changes probably precludes its development as an effective exhaust gas meter. Further tests are planned for its response time and for its sensitivity to exhaust gas composition changes.

PERFORMANCE OF MOTOR VEHICLES USING DIFFERENT FUELS

One possible solution for the reduction of pollutants from internal combustion engines is the use of gaseous fuels such as natural gas (CNG) or propane (LPG). The best application for the use of these fuels appears to be with fleet operators. The Federal Government operates between 300,000 and 400,000 vehicles, which makes it an excellent candidate for using dual-fuel systems.

A laboratory investigation conducted at the Bureau by Drs. David Didion and James Hill of the Thermal Engineering Systems Section determined the power output and pollutant levels of two U.S. Postal Service vehicles equipped with dual-fuel systems. In work sponsored by the Postal Service, the vehicles were run at simulated road conditions in an environmental chamber at temperatures from 18 °C to 43 °C (0 °F to 100 °F). Substantial reductions in the amounts of hydrocarbons, carbon monoxide, and nitrogen oxides were observed when gaseous fuels were used. Details were reported in the August issue of DIMENSIONS/NBS.[2] □

[1] Additional information is available from the Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C. 20234.

[2] Comparative Performance of Motor Vehicles Operated on Gasoline, Compressed Natural Gas, and Propane, DIMENSIONS/NBS **47**, No. 8, p. 188 (Aug. 1973).

OCCUPATION-RELATED AIR POLLUTANTS

Threshold limit values have been set for crystalline silica in respirable dust. NBS is evaluating analytical techniques that could be used to monitor the exposure of coal miners to low levels of this dust.

INCREASING attention is being focused on industrial air pollutants. Many of these pollutants have been known to reach dangerous levels and workers constantly subjected to them have been found to display a higher incidence of certain diseases than those workers who are not exposed to such conditions.

To help improve the situation, Congress passed the Occupational Safety and Health Act of 1970. NBS is currently working with the National Institute for Occupational Safety and Health (NIOSH), a part of the Department of Health, Education, and Welfare, on two projects to improve the systems used for monitoring these pollutants.

REFERENCE STANDARDS FOR INDUSTRIAL HYGIENE

A wide variety of analytical measurements must be made to protect millions of workers and to fulfill the requirements of the Occupational Safety and Health Act of 1970. Industrial atmospheres must be monitored for toxic or hazardous gases,

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OCCUPATION *continued*

vapors, and particulates, and clinical examinations of blood and urine are also required. Several hundred toxic or hazardous materials have already been identified or are under investigation, and the list will surely grow.

NBS, under the sponsorship of NIOSH, is actively engaged in a program to provide analytical reference standards, calibration procedures, and method-evaluation studies. Experimental work is underway by Dr. E. Scheide and coworkers in the Analytical Chemistry Division to develop and produce gas calibration systems, filters containing hazardous inorganic substances, analytical standards for organic solvent vapor analysis, and blood and urine reference materials.

Studies involve:

- development of analytical standards needed for atmospheric analysis of the occupational environment. Simulated filters containing the toxic materials lead, cadmium, tin, zinc, manganese, beryllium, and quartz are being produced.
- preparation of analytical standards for biological materials and/or body fluids. Test samples of lead in blood and mercury, selenium, arsenic, copper, nickel, chromium, and fluorine in urine are being developed.
- generation of analytical standards for the determination of mercury vapor in the occupational environment. Tubes containing activated charcoal on which known amounts of mercury have been deposited are being produced.
- development of analytical standards for the determination of organic solvents in the occupational environment. This work involves the production of charcoal tubes on which certified quantities of seven organic vapors have been deposited.
- production of contaminant generation systems for the certification of portable gas and vapor sampling instruments. Some of these contaminant generation systems are: toluene (2.4-diisocyanate). mercury vapor. methane. nitric oxide. ammonia. sulfuric acid vapor. and hydrogen fluoride.

NBS is working to improve the systems used to monitor pollutants in industrial atmospheres. (Photo courtesy of the National Institute for Occupational Safety and Health.)

QUANTITATIVE X-RAY ANALYSIS OF QUARTZ IN RESPIRABLE DUST

The present occupational safety and health standards accepted by the Department of Labor define threshold limit values (TLV) for a great many substances, among which are the crystalline forms of silica in respirable dust. In cooperation with NIOSH. work was undertaken by Dr. A. Perloff, Dr. F. A. Mauer. and C. R. Hubbard of the Bureau's Inorganic Materials Division to establish the usefulness and limitations of x-ray diffraction as an analytical tool for the quantitative analysis of microgram quantities of quartz.

Improved techniques and ventilation conditions in the hard rock mining industry appear to have reduced the occurrence of silicosis in miners, compared to its epidemic proportions a few decades ago. TLV for crystalline silica in respirable dust have been set at levels designed to keep exposures below those which lead to the development of silicosis. There are, however, still questions as to whether these levels provide an adequate margin of safety. So, measurements must be made of individual exposures over long periods of time. This involves a huge number of measurements and requires a reliable, accurate, and reproducible analytical technique sensitive at low levels.

Studies by the Bureau's Inorganic Materials Division indicate that of the three commonly used techniques for microanalysis of quartz dust—wet chemical. infrared absorption. and x-ray diffraction—x-ray diffraction appears to have the best potential for meeting these requirements. NBS investigations covered both the conventional x-ray diffraction technique (fixed wavelength and variable angle) and the newer energy dispersive technique (fixed angle and variable wavelength).

Results to date indicate that the conventional x-ray diffraction technique for quartz can give the needed sensitivity and accuracy with specially designed filter holders and 25-mm diameter filters for air-deposited samples, which means upgrading the current techniques. Most commonly available diffraction equipment appears to be equivalent and any reasonable choice of silts should be satisfactory. The researchers report that the energy dispersive system is not a feasible alternative technique for the quantitative analysis of respirable quartz dust at the low levels of the present TLV requirements. □

TECHNIQUES AND EQUIPMENT

TODAY'S air measurement science is yet a long way from perfection. The ambient measurement of SO_2 is a good example of the problems being encountered. The current annual average ambient air primary regulatory level for SO_2 is 80 $\mu g/m^3$ (30 ppm); the 24-hour average air primary regulatory level is 365 $\mu g/m^3$ (140 ppm).

Results of a collaborative study of the reference method for the determination of sulfur dioxide in the atmosphere are revealing.[1] Although it is impossible to summarize the complicated statistical analysis in a single sentence, the following quotation is noteworthy: "At a level of 100 $\mu g/m^3$, a difference [between a single measurement made by one laboratory and one made by a second laboratory] of less than 100 percent is not detectable."

Similar problems exist in the measurement of emission levels from automobiles. In a progress report made by General Motors to EPA.[2] GM claimed that the "...1972 Federal test at today's emission levels is on the order of plus or minus 25%. Our experience with this procedure in measuring 1975 prototype cars indicates that variation can be as much as plus or minus 50%."

Several examples of the approaches being taken by Bureau personnel to solve some of these problems are discussed below.

SULFUR DIOXIDE DETECTOR

A sulfur dioxide pollution monitoring device, in which several manufacturers have shown an interest, has been developed by Drs. Hideo Okabe and Joseph Ball of the Bureau's Physical Chemistry Division and Paul Splitstone, a guest worker from Alma (Michigan) College.[3] The first commercial model based on the work of Dr. Okabe and associates has been built by Celesco Industries of Van Nuys, Calif., and was presented to Dr. Richard W. Roberts, NBS Director, during the August 17, 1973, seminar.

The NBS detector. based on the measurement of the fluorescence of SO_2 in air. is rapid. continuous. nearly specific to SO_2. and linear in response up to 1,600 parts per million.

The most obvious application of the new device is in the monitoring of smokestack gases. About 80 million tons of SO_2 are released into the atmosphere each year, mainly through the burning of sulfur-bearing coal and oil and through such industrial processes as oil and metal refining. Some 200,000 industrial stacks may need to be monitored as the Clean Air criteria go into effect. Concentrations as low as a few parts per million are known to cause

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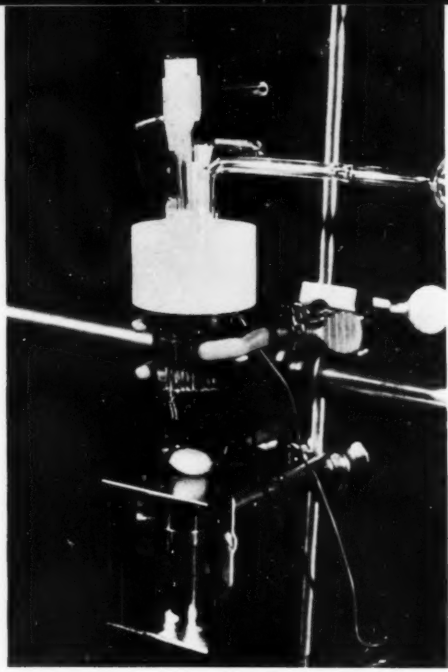
Dr. Betsy Ancker-Johnson (seated), Assistant Secretary for Science and Technology, inspects the new portable monitoring instrument that was developed as a result of original research by NBS photochemist Dr. Hideo Okabe. Also present are, from left foreground, Dr. R. Chuan and Dr. P. Mahadevan, Celesco scientists who developed the instrument, R. G. Vande Vrede, president of Celesco Industries, NBS Director Roberts, and Dr. Okabe.

TECHNIQUES *continued*

breathing difficulty, kill plants, leach limestone, and degrade paper and leather.

Dr. Frederick Schwarz and Julian Whittaker recently extended the lower limit of detection of the monitor to 2 ppb for a measuring time of 1 minute. The instrument is thus capable of routine measurements of ambient levels of SO_2 in regions relatively free of sources of SO_2. The detector has the potential of substantially improving the accuracy of measurements upon which the EPA primary and secondary regulatory levels are based.

The technique for resonance fluorescence, which was successful for the determination of SO_2, has been applied with initial success to nitric oxide. So far, the instrument has shown a linear response in the part-per-million range.



Coulometric cell used to make absolute NO_x measurements.

SIZE DISTRIBUTION OF PARTICULATE MATTER IN AIR

Dr. Claude Gravatt of the Polymers Division has developed a laser instrument that determines the size distribution of particulate matter in air in essentially real time by a forward lobe light scattering method.[4] The basic concept involves the simultaneous measurement of the intensity of light scattered by a single particle at two small scattering angles. The ratio of the two intensities is a direct measure of the size and is fairly independent of the index of refraction of the particle.

Techniques have been found that extend the lower limit of size determination to 0.05 μm. This may permit some degree of compositional characterization of the particle. The size range of most interest for lung interaction, 0.05 μm to 5 μm, is relatively easy to detect by light scattering if moderately powered lasers are employed as sources.

A prototype instrument has demonstrated the measurement of the size distribution in air of particles in the size range of 0.05 μm to 5 μm. In response to the success of this instrument, EPA is funding the construction of a portable version of this apparatus by the Bureau's Measurement Engineering Division.

Other than forest fires, according to the EPA, the main sources of particulate pollution are coal-burning incinerators, industrial furnaces and power plants, and some manufacturing and industrial processes. In addition to its obvious potential in air pollution monitoring, the device may find wide application in general aerosol studies, in smoke detector investigations, and in studies of the physiological effects of particulates.

ABSOLUTE COULOMETRIC DETERMINATION OF NO_x

A novel absolute technique for the determination of the NO_x content of SRM's and calibrating gases and possibly for atmospheric monitoring is being investigated by Dr. George Marinenko and Dale Friend of the Analytical Chemistry Division. The technique may be called a flux-balance method in which the NO_x, after reduction to ammonia, is coulometrically determined and related to a simultaneous measurement of the gas flow.

All samples in the 100 to 0.1 percent NO concentration range were analyzed by injection of a known volume of gas into the H_2 stream and titration of the absorbed ammonia. Below 0.1 percent NO gas samples were continuously injected at a known rate and the flux-balance method of analysis was employed.

The principle of the flux-balance method is as follows: the electroactive species (NH_3), which is equivalent to NO in the unknown, enters the coulometric cell, is absorbed by the electrolyte solution, forms NH_4OH, and consequently produces the pH change in the solution. This effect is electrochemically counteracted by the generation of H^+ at a platinum anode. When the electrical current is of such magnitude that the pH of the solution remains constant, while the analyzed gas is flowing through the system at a constant rate, the "flux balance" has been achieved. The ammonia flux is equal to the electrogenerated proton flux.

The *a priori* calibration of the total gas flux through the capillary

at a given differential pressure and temperature enables the evaluation of the mole fraction of NO.

Although the electrical flux can be easily maintained constant, the short-term fluctuations in the composition of a mixed gas stream are far more difficult to control. To circumvent the problem, time averaging by integration is employed.

The advantages of the flux-balance method for low-level NO measurements are: (1) the system is continuously flushed with the unknown mixture; therefore any surface losses that might be taking place on the walls of the gas train can be eliminated by conditioning the system for sufficient periods of time to affect saturation; and (2) if sufficient sample is available, measurements can be performed over long time intervals resulting in a better time averaging value.

The data obtained for NO-N_2 mixtures confirm the absence of any systematic measurement error. Nitrogen oxide determinations are possible using coulometry for gas samples containing from 100 percent NO down to 2 ppm. The precision of measurement for 100-0.1 percent NO samples is on the order of 0.6 percent. At the 2 ppm level, the precision is 3 percent. Using the flux-balance method, NO at sub-ppm concentration levels can be determined.

PYROLYTIC METHODS USED TO PRODUCE STANDARDS

Some pollutant molecules are so reactive that they cannot be stored over extended periods of time. To get around this problem, Dr. Wing Tsang of the Bureau's Physical Chemistry Division and Dr. Douglas Cornell of Fairleigh Dickinson University have demonstrated that pyrolytic reactions can be used.

Suitably chosen parent compounds, when heated, break down into equimolar amounts of pollutant and nonpollutant molecules. For example, when oxetane, a relatively stable molecule, is heated it breaks down into exactly one molecule of formaldehyde and one molecule of ethylene. In use, the oxetane molecule would be passed through a heated tube, and the amount of ethylene (a gas easy to measure) would be monitored. Knowing the amount of ethylene is equivalent to knowing the amount of formaldehyde, which is the information necessary to calibrate an instrument.

SO_2, NO, and the lower aldehydes over a wide range of concentrations have thus far been produced by this technique. Among the advantages of this technique is its potential for generating accurately known and adjustable concentrations of pollutant under easily controlled conditions. The method also affords safeguards against calibration errors in routine field determinations.

LASER APPLICATIONS TO AIR POLLUTANT MEASUREMENT

Effective measurements of air pollutants require a number of different simple. inexpensive. sensitive, accurate, reliable, and, for many applications, fast detectors. For a number of different applications a variety of laser-based detection schemes have been developed or are now under development at the Bureau.

All techniques take advantage of the laser as a high-resolution, high-intensity source replacing complex and cumbersome high-resolution spectrometers. They also take advantage of laser spectroscopic techniques, eliminating the need for large and complex sampling cells and optical alignments.

An optoacoustic detector has been built for the measurement of NO. Using a CO laser operating at 5.21 μm, Drs. A. Kaldor and R. Keller and coworkers in the Optical Physics and Physical Chemistry Divisions have been able to detect 0.4 ppb of NO, and operating the laser at 6.15 μm they can detect 0.1 ppb of NO_2. The optoacoustic detector is based on the concept that, after the vibrational excitation of a molecule in about 100-1000 collisions, the vibrational energy is equilibrated with the kinetic energy of the system. This causes a very minute pressure change within the cell that can be detected with extreme sensitivity by a microphone. Only molecules in resonance with the absorbed radiation can yield the pressure signal to be detected by the microphone. The modulation of the pumping radiation produces pressure pulses that are synchronously detected. One important advantage of the detector is that for both NO and NO_2 a single laser will suffice, and a single calibration point will calibrate the system for both species.

Another measurement technique developed at NBS by Dr. A. G. Maki is based on the unique properties of NO and NO_2. Both of these molecules are strongly paramagnetic. Using the Zeeman effect it is therefore possible to shift the molecular absorption of either molecule into near coincidence with a CO laser line with a dc magnetic field and to modulate the molecular absorption by a superimposed ac magnetic field. rather than modulating the incident laser light, as is done in conventional absorption spectroscopy. The resultant detector, demonstrated for NO and presently under test for NO_2, is a linear, specific detector for NO with high sensitivity. The Zeeman technique does not suffer from interference from other molecular species or from particulates. □

[1] Collaborative Study of Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosanile Method), Southwest Research Institute, Houston, Tex., p. B-18 (Sept. 1971).

[2] Progress Report by the General Motors Corp. to the U.S. Environmental Protection Agency (March 12, 1971).

[3] Sulfur dioxide monitor, Nat. Bur. Stand. (U.S.) Tech. News Bull. **46**, No. 10, Oct. 1972.

[4] Determination of particle size in real time, Nat. Bur. Stand. (U.S.), Tech. News Bull. **46**, No. 12 (Dec. 1972).

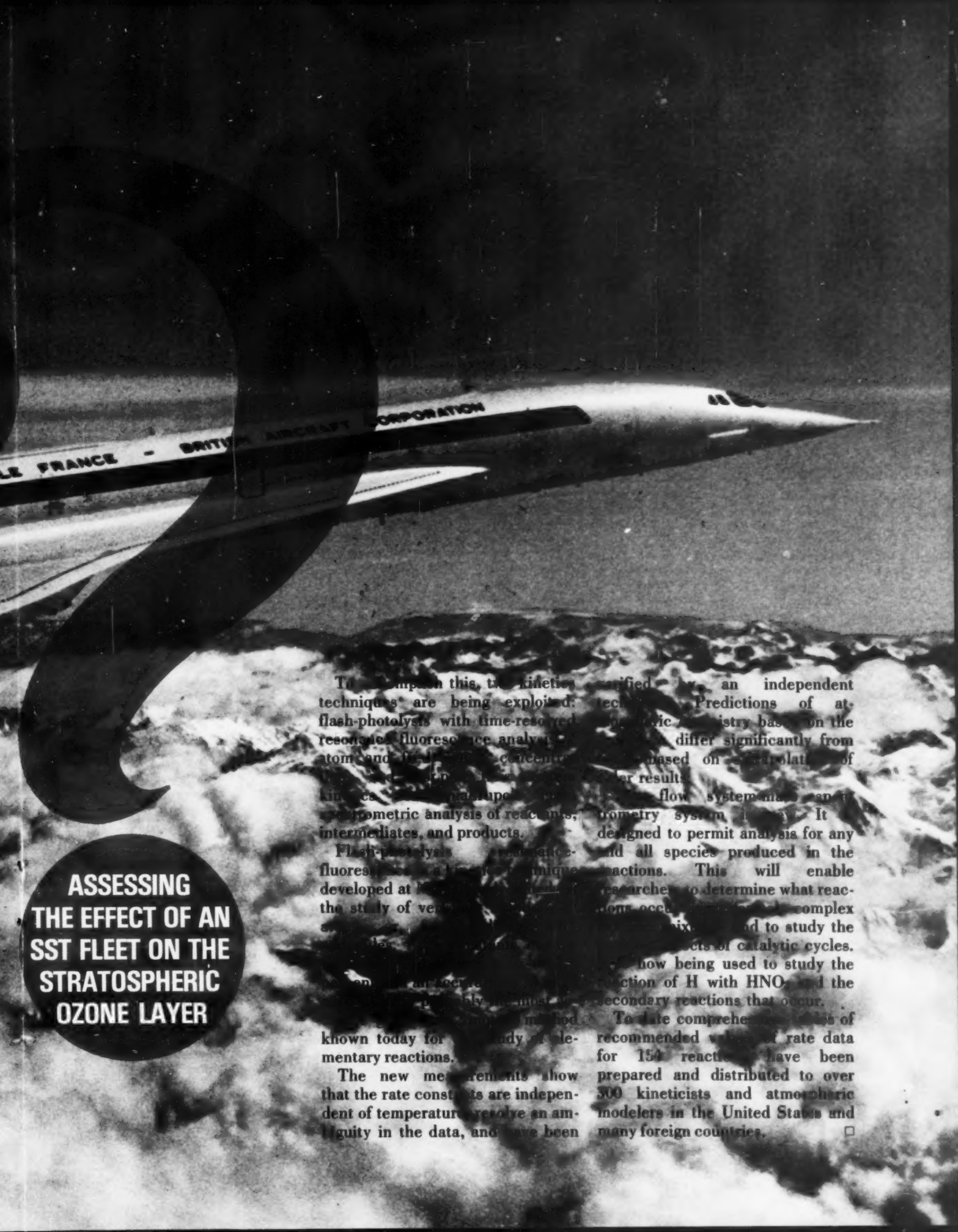
STRATOSPHERIC AIR POLLUTION

OZONE in the [illegible] highest atmospheric layer, the stratosphere, controls the amount of ultraviolet (uv) light reaching the surface of the earth. A decrease in the amount of ozone would permit more short wavelength uv to reach the earth, which may be detrimental to living plants and animals, including man, as well as other materials.

A 3-year study by the Climatic Impact Assessment Program of the Department of Transportation is probing this question because of the potential harm to the ozone layer which might be caused by the use of Super Sonic Transports (SST) now being built abroad and still under discussion in the United States. The purpose of the DOT program is to gather enough data to permit a prediction to be made about the ecological effects of an SST fleet.

Assessment of this potential perturbation can only be made by numerical mo[illegible] accurate rate constants, [illegible] yields, and absorption c[illegible] as input. Members of the NBS Physical Chemistry Division under the leadership of Dr. David Garvin are supplying basic data needed for the models to be used to make the prediction. These data are based partly on reanalysis of existing measurements and partly on new experiments. The measurement program is designed to fill in gaps in the data base that are revealed by analysis. The product will be new tables of [illegible] chemical processes in the stratosphere.

The experimental portion of the program has two goals: (1) to obtain accurate rate constants for reactions of obvious importance (i.e., to improve the crucial data) and (2) to measure rate constants for reactions not studied or for cases where the data conflict.



ASSESSING THE EFFECT OF AN SST FLEET ON THE STRATOSPHERIC OZONE LAYER

To [illegible] this, t[illegible] kinetic techniques are being exploited: flash-photolysis with time-resolved resonance fluorescence analysis [illegible] atom and [illegible] concentr[illegible] [illegible] kinetics [illegible] mass spectrometric analysis of reactants, intermediates, and products.

Flash-photolysis [illegible] resonance-fluoresc[illegible] a [illegible] technique developed at [illegible] the study of ve[illegible] [illegible] known today for [illegible] study of elementary reactions.

The new me[illegible]rements show that the rate const[illegible]ts are independent of temperature, resolve an ambiguity in the data, and have been [illegible]ified by an independent tech[illegible]. Predictions of atmospheric [illegible]istry bas[illegible] on the [illegible] differ significantly from [illegible] based on [illegible] of [illegible] results.

[illegible] flow system mass spectrometry system [illegible]. It [illegible] designed to permit analysis for any and all species produced in the reactions. This will enable researchers to determine what reactions occ[illegible] complex [illegible] and to study the [illegible] of catalytic cycles. [illegible] now being used to study the reaction of H with HNO_3 and the secondary reactions that occur.

To date comprehe[illegible] of recommended [illegible] rate data for 154 reacti[illegible] have been prepared and distributed to over 300 kineticists and atmospheric modelers in the United States and many foreign countries. □

STANDARD REFERENCE
POLLUTANTS

ONE of the Bureau's important functions is to develop and/or certify Standard Reference Materials (SRM's). SRM's have been used since 1906 to calibrate measurement systems and to provide a central basis for uniformity and accuracy of measurement. At present more than 800 SRM's covering a wide range of chemical and physical properties are available, including industrial materials (tin, steel, rubber, glass, etc.), biological standards. radioactivity materials. and analyzed gases.

The Measures for Air Quality program is actively engaged in providing a series of SRM's to serve as calibrants, test mixtures, and standardization materials for environmental analytical instrumentation and methodology. For example, the sulfur dioxide permeation tubes (SRM's 1625-1627) are cited by EPA as the standard for the calibration of the reference method for the determination of SO_2. Other SRM's that are of particular interest to those measuring pollutants are: sulfur in residual fuel oil (SRM's 1621-1623); sulfur in distilate fuel oil (SRM 1624); powdered lead based paint (SRM 1579); mercury in coal (SRM 1630); and sulfur in coal (SRM 1631). Analyzed gases, SRM's 1601-1611 and 1613, are used for the calibration of equipment used to measure various components in gas mixtures, in some cases particular atmospheric pollutants. These range from carbon dioxide in nitrogen to hydrocarbons in air. Several other SRM's for use in pollution monitoring are currently under development.

TRACE ELEMENT STANDARD REFERENCE MATERIALS

The extent of emissions of trace metallic elements from the combustion of fossil fuels by industries, power plants, and home heating is not completely known. The only comprehensive studies to date have been made of the emissions of oxides of sulfur, nitrogen, and carbon and, to a lesser extent, mercury. To determine the extent of the emission of these trace metals and to define problems associated with those emissions, data on the trace element content of fossil fuels and on the extent these trace elements are expelled from stacks and exhausts will be essential.

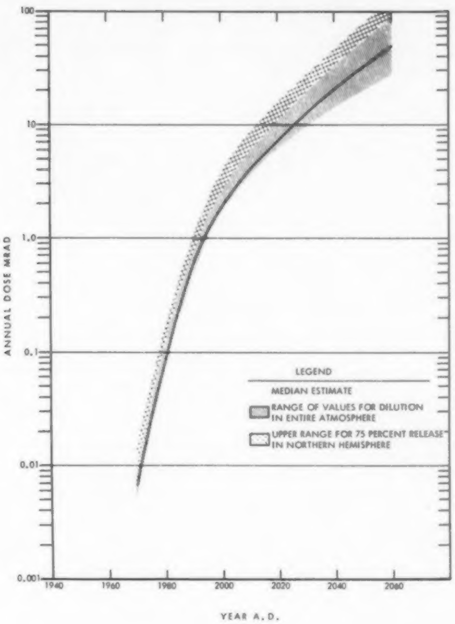
Trace metals receiving highest priority by EPA are: mercury, selenium, arsenic, cadmium, zinc, beryllium, chromium, and lead. In a joint program with EPA, the Bureau is in the process of certifying fossil fuels such as coal, fly ash, and fuel oil as SRM's. These SRM's will provide analysts with standards in matrices similar to those they are analyzing, helping establish some degree of accuracy and precision in monitoring emissions of fossil fuel combustions. And they will assist EPA in setting regulations for trace element content of fuels.

Samples of coals and fly ashes were collected from electric power plants in Alabama, North Carolina, Kentucky. West Virginia. and Montana. The coals and fly ashes were sieved to prevent segregation and to limit particle size. After sieving they were mixed in a double-coned blender and then bottled. Samples were tested for homogeneity by neutron activation analysis of randomly selected samples. Replicate analysis indicated that the fossil fuels were homogeneous within $\pm$2-3 percent.

Analyses of the fossil fuels were performed by NBS and an EPA-sponsored "round robin" to provide certified values for the various trace elements. Samples were sent to 68 selected laboratories to obtain a broad spectrum of the analytical community—industries, universities, and government. Results from this round robin are still being evaluated; however, NBS investigators have made several comments on the state of analysis of fossil fuels as perceived from data obtained from the round robin and data in the literature:

- The present state of analysis is "terrible."
- Few results, especially those reported in the literature, may be believed unless adequate calibration standards in the same matrix are available.
- Meaningful and accurate data can be obtained only if full dedication is given to analyzing "real world" samples. □

ACTIVITY OF
RADIOACTIVE GASES



Estimated annual dose from krypton-85 1970-2060

TRITIUM, found mainly as water, and carbon-14, present in the form of carbon dioxide, have always been produced by natural processes. But the environmental inventory of each is increasing due to man's activities. Added to these are long-lived krypton-85, which is now present in the environment as a result of various nuclear fission activities, and shorter lived radioactive noble gases.

Problems associated with these radioactive gases have been accentuated by the rapid increase in the use of nuclear power coupled with newly instituted regulations of the Atomic Energy Commission limiting all radioactive releases to levels "as low as practicable." According to several estimates, by the year 2060 we, or our grandchildren, may closely approach the maximum permissible concentration of krypton-85 in air—170 m-rad per annum.

Hugh DeSpain and Sam Garfinkel* of the Center for Radiation Research have developed a fast and accurate technique for calibrating monitors for measuring radioactive argon-41 effluent being expelled from the stack of a nuclear reactor. Argon-41 is one of the most active radioisotopes released to the environment.

In the NBS procedure natural argon is sealed in a polyethylene tube and irradiated in a reactor to yield argon-41 by the (n,γ) reaction. The argon-41 is assayed by comparison with sodium-22 and injected into an ionization chamber, together with air at atmospheric pressure, to calibrate the chamber. The chamber can then be filled with a sample of stack gas and the argon-41 activity measured with confirmatory measurements of the half life.

NBS length-compensated internal gas counters used in the proportional or Geiger regions have been the principal means for producing radioactivity standards of ^{3}H, ^{14}C, ^{85}Kr, ^{131m}Xe, and ^{133}Xe. The Bureau's isotope separator has been used to prepare ^{133}Xe standards—free of ^{131m}Xe—from reactor off-gas samples.

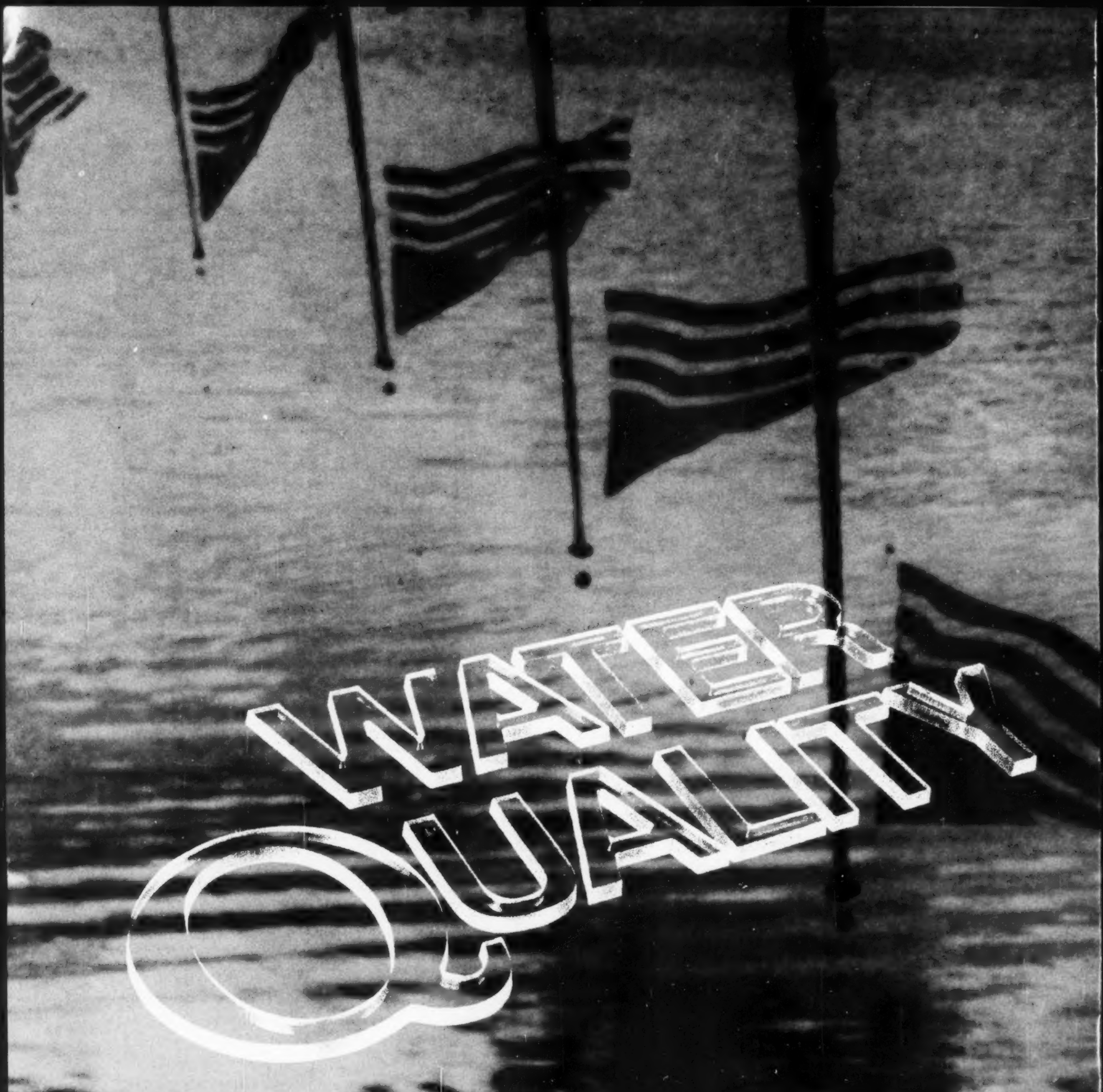
A set of length-compensated internal gas counters used by Dr. W. B. Mann and coworkers in the Bureau's Applied Radiation Division consists of three counters of different lengths but with identical end supports for the central anode wire. Taking the difference in count rate for a given difference in volume it is possible to compensate for the decrease in electric field strength at the ends of the counters. Differential volumes are measured by closing one end of each vertically supported counter with a teflon slab and filling the counter with water until the surface just touches a tungsten point. By using a pycnometer made from a plastic baby doll bottle, the mass of water can be measured to about 10 mg in 100 to 200 g. In dispensing radioactive solutions they give precisions in the order of 5 μg for a 30-mg drop.

The NBS gas counting system consists of one set of stainless steel and one set of copper length-compensated counters. Count-rate data at different cathode voltages and gas pressures are fed simultaneously from all six counters into an on-line computer used as a multichannel pulse-height analyzer.

The Bureau's point-source krypton-85 standards were calibrated using the method of coincidence counting of the x and gamma rays from strontium-85 rather than by the gas counting method. □

* deceased

WATER QUALITY



The case for controlling the amounts of toxic materials dumped into our natural waters is a simple one. The public is aware of such horror stories as the Minimata, Japan, disaster in which 52 people died from mercury poisoning and 150 more suffered severe disorders. Fish taken from polluted waters were the source of the poisoning.

THE effects of ingesting a toxic substance are not necessarily immediate or easy to determine. In Minimata, 23 babies showed signs of a cerebral palsy-like disease; their mothers had eaten contaminated fish but were themselves apparently healthy. The fact that the mothers appeared healthy at that time does not assure that they will not suffer disorders in the future related to their intake of mercury. Delayed symptoms may appear at a later time even if they ingest no more mercury. Or without considerable alteration in their diets or the eradication of the poison from the environment. the women could also fall prey to the possible cumulative effects of the poison.

NEED FOR ACCURATE MEASUREMENT METHODOLOGY

Less spectacular but of consequence to large segments of a population are the subclinical effects of mercury. Minute trace levels present in water and ingested by organisms are in turn eaten by man. The result is a build-up of the poison in the human body. This build-up, it is reported, can cause delayed neurologic and intellectual damage. No systematic studies of such effects have been made, but it is clear that the development of a more accurate measurement methodology for mercury is an essential prerequisite to such studies.

A means of accurate measurement is essential to the analysis and application of knowledge about the underlying chemistry of mercury and other pollutants. Studies are now underway by NBS scientists to determine how relatively harmless inorganic mercury becomes transformed microbially into lethal methyl mercury. This process occurs when inorganic forms are changed chemically by organisms present in our waterways. The transformation can also occur by chemical reaction with other heavy metals such as lead and tin with or without the intervention of biological material.

WIDE RANGE OF POLLUTANTS

Mercury has been discussed only as an illustrative example. It may be the most dangerous of the heavy metals, but it is not the only culprit threatening the environment. In addition to the toxic metals, radioactive effluents from nuclear reactors and organic compounds (such as hydrocarbons contained in oil spills) pose critical problems that demand immediate attention.

In response to the critical need for water pollution abatement, Congress passed the Water Pollution Control Acts Amendments of 1972. The following excerpts from that piece of legislation present the national goals:

Title I. Section 101(a)

- It is the national goal that the discharge of pollutants into the navigable waters be eliminated by 1985.
- It is the national goal that wherever attainable an interim goal of water quality...be achieved by July 1. 1983.
- It is the national policy that the discharge of toxic pollutants in toxic amounts be prohibited.

EPA and the Atomic Energy Commission are charged with the responsibility of setting and enforcing regulations that will result in the achievement of these goals. The director of EPA is also entrusted with responsibility for conducting research on pollutants and securing methods of measuring and monitoring those substances.

It is important to realize that the government does not wish to repudiate technology. It does wish to establish and maintain a safe environment. Inaccuracy in measurement makes the job of controlling pollution more difficult. Without reliable and generally accepted measurement systems pollutants cannot be accurately detected and monitored. It also necessitates overdesign of pollution control systems at great cost to industry and, ultimately, the consumer. When we consider that some $4 billion annually is expected to be spent in the next decade in capital investment in water pollution control, it is easy to recognize the importance of economical design of controls. Based on this estimate a 10 percent overdesign will cost $400 million per year and a 5 percent overdesign will cost $200 million.

NBS INVOLVEMENT

NBS, through the extended MAQ program, works to provide basic scientific knowledge and measurement expertise essential to Federal agencies, State and local governments, and industry. The Bureau is considered a logical agency for the establishment of the required measurement standards, both in chemical pollution and radioactivity, because of its reputation for integrity and impartiality. With NBS filling this role, EPA, AEC, the State and local governments, and industry can all have confidence that the water measurement system is consistent and credible.

To that end, the Bureau has set the following high-priority projects:

- Analysis of trace contaminants in water. (This includes measurement research aimed at development of Standard Reference Materials, and the development of an accurate means of measuring water flow velocity and pollutant masses moving past a boundary in a flowing stream.)
- Study of mechanisms of transformations of metals in the environment.
- Development of accurate radioactivity-in-water measurements for both ambient water and reactor effluent.
- Development of measurement methods for nonmetallic inorganic and organic pollutants. □

TRACE METAL **CONTAMINANTS**

DETERMINATION of trace levels of toxic metals in natural waters is one of the major concerns in the NBS water quality program. Previous success in accurately determining minute amounts of these materials has been limited. Determination of accurate measurement methods usually leads to the development of SRM's to be used to test and calibrate trace level monitoring methods and equipment.

TRANSFORMATIONS OF HEAVY METALS

Drs. Frederick Brinckman, Warren Iverson, and Philip LaFleur of IMR are involved in a joint investigation of chemical, biological, and other mechanisms operative in natural water systems for mobilization and transport of heavy metals. Their particular concern is the transformation of inorganic mercury into highly toxic forms. The project currently seeks to identify specific transformation reactions of mercury compounds, both chemical and biological, and to determine what rates of mercury transport exist or are possible as a consequence of these reactions. One objective is to develop the methodology required for these measurements. This step will lead to the generation of referee methods and Standard Reference Materials.

The transformation project should provide improved understanding of the mechanisms and rates of mercury cycling in the environment and improved experimental techniques. Because the work centers around the Chesapeake Bay (Md.) area, results will be of special interest to industries in that and similar regions.

The first phase of the program involves selection, acquisition, and analysis of field samples of sediment and water which are being analyzed for total mercury and organic mercury. Nuclear magnetic resonance (NMR) and mass spectrometry are being used to characterize the kinds of organic structures bound to metallic or inorganic mercury. Parallel experiments will be designed to detect other possible methylation pathways.

Project activities to date have resulted in publication or presentation of several aspects of the work:

1. "Biodegradation of Phenylmercuric Acetate by Mercury Resistant Bacteria," J. D. Nelson, W. Blair, F. E. Brinckman, R. R. Colwell, and W. P. Iverson, *Appl. Microbiol.*, accepted for publication.
2. "Transmethylation of Heavy Metal Ions in Water," F. E. Brinckman and K. L. Jewett, 8th Middle Atlantic Regional Mtg. of the Amer. Chem. Soc., Washington, D.C., Jan. 1973. Abstracts of Papers. p. 52.

POLAROGRAPHIC ANALYSIS

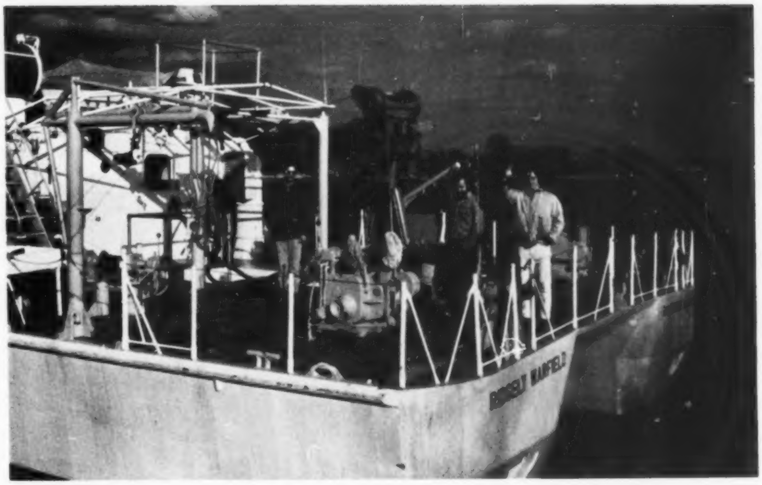
NBS chemist E. June Maienthal of the Electrochemical Analysis Section, Analytical Chemistry Division, is working with a technique called cathode ray polarography. Briefly, polarography is a procedure for determining the concentration of an ion in solution by measuring its electrolysis current at a known voltage. One of the electrodes is a glass capillary which extends into the solution being analyzed and from which small drops of mercury are periodically emitted. From the current-voltage curve produced during electrolysis both the species and

concentration of a material under analysis may be determined.

The use of this technique has precipitated the development of improved methods for the determination of a number of metals as well as organic substances such as nitrilotriacetic acid (NTA) in various water samples. Similar methods have also been applied to the monitoring of metal content of particulates collected under different types of conditions. orchard leaves. and lunar soil and rock.

A cooperative program with EPA for the study of sampling and analysis of blood, bone, liver, and other tissues has evolved from the present work.

Polarographic methods developed at NBS have unique capabilities in selectivity. sensitivity. and accuracy and have provided reliable analytical data in many environmental problems. Their accuracy has been verified through collaborative work with competent chemists using a number of different techniques on many materials.



Members of the research team on transformations of heavy metals aboard vessel used in field work.

ISOTOPE DILUTION

Research chemist Robert Alvarez of the NBS Office of Standard Reference Materials, in cooperation with Paul J. Paulsen of the Isotopic Analysis Section. developed a stable isotope dilution procedure using the spark source mass spectrograph for simultaneously determining a dozen trace elements in river water samples. The elements determinable at concentrations down to part–per–billion levels include mercury, cadmium, lead, and copper.

This method can be applied to the development of natural water SRM's. Certain steps must yet be taken before actual work can begin on these much-needed materials:

- Communication with private and government organizations to establish acceptance of SRM's.
- Definition of the composition of the analytical system with respect to pollutants and their concentrations. (Because of the complexity of natural water systems, synthetic water SRM's having the elemental composition of natural water but without particulate matter is recommended. The trace pollutants should be at or near critical or proposed specification values. A pure water SRM with only one or two pollutants is of interest but without the other elements normally found in natural water it would be too simplistic an approach.)
- Use of at least two analytical methods with the foible of one method being the forte of the other.
- Maintenance of the integrity of a liquid sample. Certified concentration of the pollutants must not change. Issuing the fresh water SRM's in a frozen state might solve the problem.

The distribution of these fresh water SRM's would encourage interlaboratory testing, enabling analysts to determine the accuracy of existing methods and to develop more reliable field and referee methods. Because laboratories of regulatory agencies and of industry would both be using the SRM's in their test procedures, more meaningful and acceptable Federal specifications could be issued.

To determine significant changes in trace elements, comparative analytical techniques are most effective. In these measurements the SRM's would serve as tangible and immutable meter sticks. At present evaluations of the effectiveness of abatement measures are controversial. □

Typical Matrices Analyzed by Cathode Ray Polarography

Metals
- High-Temperature Alloys
- Steels, Cast Irons
- Brasses, Bronzes
- Lead-Base Alloys
- High-Purity gold, platinum, zinc, and selenium

Glasses, Rocks, Silicates

Foods, Botanicals

Biomedical Solutions

Metallo-organics

Environmental Samples
- Air Particulates
- Waste, River Water

High-Purity Reagents

CONTAMINATION OF THE SEAS BY OIL SPILLS

Scientists in IMR are working on techniques for measuring solubilities and partition coefficients of hydrocarbons. This information should assist those involved in cleaning up oil spills.

THE fate and effect of petroleum oil and petroleum product spills in the ocean are of international importance. Crude oil and oil products spilled in nature are changed by evaporation, by solution, and by bacterial and chemical attack. Of these different processes, the most important as far as effect on marine life is dissolution.

Hydrocarbons are chemical compounds responsible for damage to marine life and, subsequently, to man. Low-boiling aromatic hydrocarbons are the most immediately toxic fraction; benzene, toluene, and xylene are acute poisons. This fraction is the most soluble in sea water.

Olefinic hydrocarbons, which are absent in crude oil but occur in refining products, are probably intermediate in toxicity between the saturated and aromatic hydrocarbons. This fraction is fairly soluble in sea water.

The low-boiling saturated hydrocarbon fraction produces insidious effects upon lower animal life, even at low level concentration. At high concentration, cell damage and death occur.[1]

Dr. Stanley Wasik and coworkers in the Physical Chemistry Division are working to develop techniques for measuring solubilities and partition coefficients of hydrocarbons. These are two important related quantities to be considered in the dissolution of hydrocarbons in the ocean.

A stable isotope dilution chromatographic method has been developed for measuring trace levels (parts per billion) of hydrocarbons in sea water and fish tissues. The technique involves adding to the sample a known quantity of a deuterated labeled material and measuring the appropriate isotope ratio by gas chromatography. The concentration of the anolyte is then determined by multiplying the known concentration of the isotopically labeled material by the isotope ratio.

Another NBS achievement in this area is an apparatus for measuring the solubility of hydrocarbons in sea water over a temperature of 0-25 °C. A known volume of the hydrocarbon ii allowed to equilibrate with a known volume of sea water by means of a pump circulating the air-hydrocarbon mixture around a closed circuit. After equilibrium is reached, a small volume of the gas phase is analyzed by gas chromatography. A known volume of the gas phase is then flushed out and the process repeated. The solubility and partition coefficient of the solute in sea water is determined from the relative peak areas of the chromatograms obtained after successive equilibria and from the volumes of the apparatus. □

[1] Blumer, M., Environmental Affairs, Vol. I, No. 1, April 1971.

RADIOACTIVE POLLUTANTS

BY December of 1973 there will be approximately 40 nuclear power plants in operation in the United States. The radioactive, artificially produced contaminants called radionuclides pose a potential threat to the environment.

To minimize the release of radioactive materials, each power plant must, under AEC and EPA guidance, maintain an extensive effluent and environmental monitoring program. A major element in these programs is the maintenance of accurately calibrated instruments for measuring radioactivity. The Radioactivity Section in the Center for Radiation Research has produced many of the standards needed for instrument calibration over the years.

Some of the water systems within nuclear power plants are contaminated with radioactive elements. The two main sources of this radioactivity are uranium fission products which escape the fuel cladding and species resulting from the activation of corrosion products.

In normal operation the level of radioactivity is controlled by routing a fraction of the total flow through a chemical purification system. Still some leakage is known to occur. Water which escapes is filtered and passed through a radioactive waste disposal system. The concentration of tritium, in the form of tritiated water, is essentially unaffected, however. Eventually some of it is discharged into the environment following dilution with return water from the condenser. Since the flow rate on this return line is often as high as a half-million gal/min it is relatively easy to achieve a dilution factor of greater than 1000 for the radioactive water discharged to the environment.

From an environmental standpoint, some of the most critical measurements are made on waste water prior to dilution. One can make measurements on chemically pure samples of moderate activity. Given the importance of these measurements, one of NBS goals has been to develop standards to calibrate the instruments used in these measurements and to get these standards to the power plants.

Of the 17 most significant fission products which might be present in reactor waste water, calibrated samples of 12 are already available from the Bureau. NBS either produces standards for these species or such materials have been calibrated in the past.

To assay a liquid mixture, at least three methods of analysis are required:

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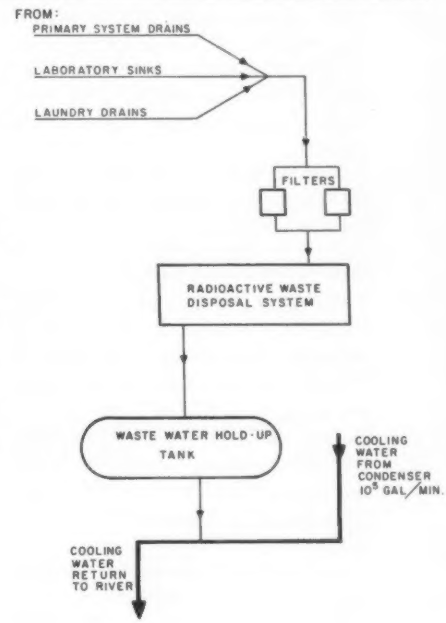
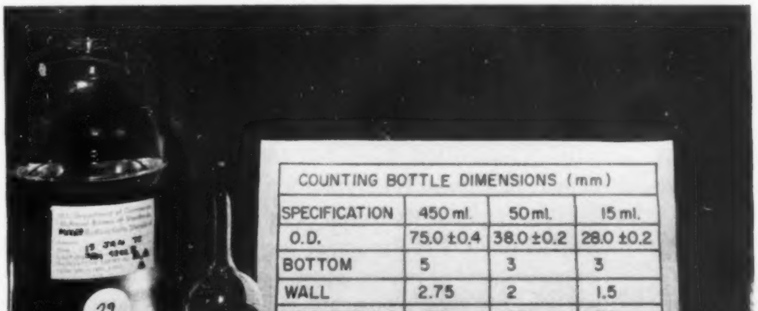
SCHEMATIC OF A RADIOACTIVE WASTE DISPOSAL SYSTEM



NBS standard counting bottles containing SRM's insure greater integrity of contents after storage.



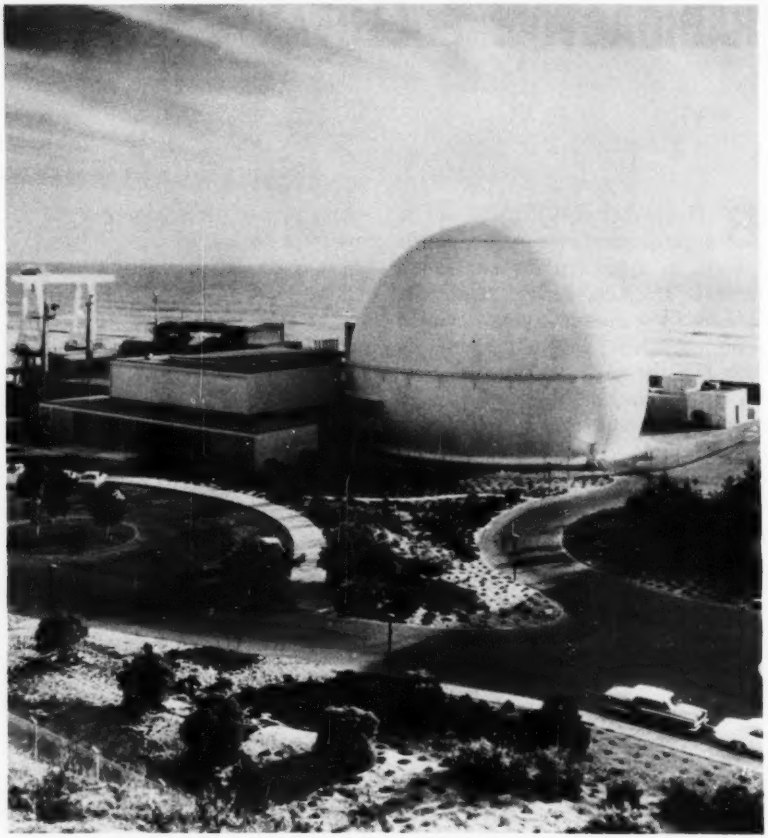
RADIOACTIVE *continued*

1. High-energy beta-particle emitters such as strontium-89 and strontium-90 must be separated by radiochemical methods. The beta-particle emission rate is measured with gas-flow proportional counters.
2. Tritium, a low-energy beta-particle emitter, must be separated from other radionuclides present, usually by distillation. Tritium activity of the distilled water is measured using liquid scintillation counting.
3. Most of the remaining species are measured directly by gamma-ray spectrometry.

DEVELOPMENT OF SRM's

Dr. James R. Noyce of the NBS Center for Radiation Research is currently completing calibration of ^{89}Sr and ^{90}Sr. In addition to separate solutions, a calibrated mixture of the two may be marketed through the SRM program. Tritiated water and tritiated toluene SRM's are available for calibrating liquid scintillation counters.

Calibration techniques or standards exist for a number of other radioactive substances including several of the gamma-ray emitting radionuclides. □



Each nuclear power plant must, under AEC and EPA guidance, maintain an extensive effluent and environmental monitoring program. (Photo courtesy of the U.S. Atomic Energy Commission.)

OPTICAL RADIATION NEWS NOTE

The Optical Radiation News (ORN) will no longer appear in DIMENSIONS/NBS (formerly the Technical News Bulletin). This feature is being discontinued as part of a major renovation in the magazine's structure.

The Optical Radiation Section is considering the distribution of a separate newsletter as a replacement for ORN. The decision will primarily depend upon an assessment of reader interest in the topics covered by ORN. Interested readers are asked to send a postcard indicating such interest to:

Dr. H. J. Kostkowski Chief, Optical Radiation Section
Room A223, Physics Building National Bureau of Standards
Washington, D.C. 20234

Highlights

NEW ETIP DIRECTOR AT NBS

Dr. Richard W. Roberts, NBS Director, has announced the appointment of Dr. Jordan D. Lewis as Director of the Experimental Technology Incentives Program (ETIP).

A former director of the Battelle Memorial Institute's Applied Technology Programs, Dr. Lewis brings to the new program extensive experience in developing new product, process, and service technologies affecting the Nation's economy.

CONSUMER PROTECTION

NBS is working with the Food and Drug Administration in optimizing the allocations of FDA's field resources (i.e., inspections, samples, collections, analyses) to maximize consumer protection for products under FDA jurisdiction. NBS is testing mathematical models of how the resources should be allocated against an empirical data base to determine the validity of the models. NBS is also designing an experiment in which various sampling plans for products within a commodity (e.g., frozen foods, canned vegetables, bakery products) can be evaluated. The study is expected to be completed within 6 months.

STANDARDS LABORATORIES CONFERENCE TO BE HELD

The National Conference of Standards Laboratories (NCSL) will hold its 1973 meeting on November 14-16, at the Bureau's Gaithersburg, Md., campus. Keynoting the conference will be NBS Director Richard W. Roberts. General Chairman for this meeting is A. J. Woodington, General Dynamics/Convair Aerospace Division, San Diego, Calif.

Discussions on instrumentation trends, dimensional measurement programs, regulatory agencies, test equipment utilization and management, and measurement problems of the small laboratory will be featured. For details contact J. M. Cameron, A345 Physics Building, NBS, Washington, D.C. 20234.

IMPROVEMENT IN MEASUREMENTS TRANSFER

Customers of the Measurement Assurance Program in calibration of mass standards now receive with their report of calibrations a full laboratory-notebook-type account of all detailed procedures followed at NBS, together with helpful suggestions and background information as to how these procedures can be used to establish control of the participants' measurement process.

A similar, but less detailed calibration report is also furnished with the service for piston gages, a widely used transfer standard for pressure. Eight different sets of coefficients are given, and the customer can select the set that will best characterize the gage for his particular purposes.

A change in the method of calibration of thread-measuring wires has resulted in a saving in costs to the customers of 20-25 percent. The new method involves the precise and statistically controlled transfer from NBS master thread wires rather than classical direct interferometric measurement. In addition to the cost savings, a reduction in overall uncertainty is achieved and a more complete documentation of measurement process behavior is provided.

NEW PORTLAND CEMENT STANDARDS

Seven new Portland Cement Standard Reference Materials have been issued, representing the culmination of an outstanding cooperative program between industry and NBS. These SRM's are essential to the cement industry in controlling the quality of the more than 400 million barrels of cement produced and sold annually in the United States.

The new SRM's, 633 through 639, replace five cement SRM's first issued in 1962 and extend the concentration range for most of the certified constituents. These cement SRM's are intended for use both in checking chemical methods of analysis and in the calibration of rapid instrumental methods of analysis.

INSTRUMENT WINS AWARD

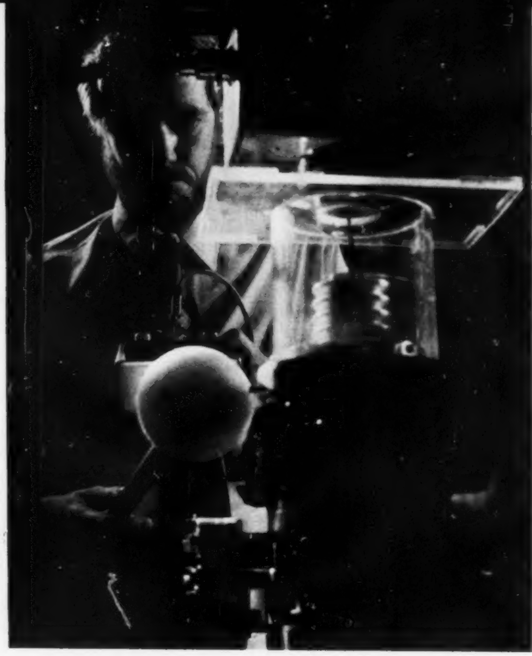
An electric energy density meter invented at the Bureau's Boulder, Colo., laboratories has been selected by Industrial Research Magazine as one of the 100 most sig-

turn page

HIGHLIGHTS *continued*

nificant new products of the year. Developed by Ron Bowman, Don Belsher, and Ezra Larson of the Electromagnetics Division, the meter is used to measure the intensity of electromagnetic energy, such as that emitted by radars, microwave ovens, and radio transmitters.

It provides easy, accurate readings of complex electromagnetic fields and can be used to test the effects of radio waves on living organisms, find leaks of energy in microwave systems, and test radar equipment for hazardous radiation.



Using the electric energy density meter, Ron Bowman, physicist, is determining if the radiation from the laboratory equipment in the foreground is intense enough to be hazardous.

CRYOGENICS IN CENTRAL AFRICA

At the request and sponsorship of the National Oceanic and Atmospheric Administration, a SQUID magnetometer was carried to Fort Lamy, Chad (Africa), by Dr. James Zimmerman to observe the interaction between the equatorial electrojet and the 30 June 1973 solar eclipse. (The electrojet is an ionospheric current of about 10^5 amperes flowing along the magnetic equator.) The SQUID was used because its sensitivity to small magnetic field changes was greater than that of any other available instrument, and it was hoped that it could resolve any fine details of the interaction phenomenon.

The expected effect was a drop in the north-south component of the earth's magnetic field due to a decrease in the current. As the ionosphere is produced in large measure by the sun's ionizing radiation, the shadow of the eclipse was expected to reduce the ionization. Results of the observation are not yet evaluated.

SMOKE MOVEMENT IN HOSPITALS

NBS will conduct a study in 10 hospitals to determine the potential movement of smoke and toxic gases in the event of fire. The study. sponsored by the Veterans Administration. will involve the use of an odorless. nontoxic. and chemically and thermally stable tracer gas (sulfur hexafluoride-SF_6) to simulate smoke movement. By using the tracer gas technique. tests can be performed during normal hospital operation without disrupting patients and employees. The simulated smoke movement will be analyzed for each of the hospitals under different ventilation and environmental conditions. Based on these analyses. NBS will recommend design criteria and operating procedures for smoke control in V.A. hospitals.

ADVANCED AUTOMATION SYSTEMS CONFERENCE

The Bureau's Institute for Computer Sciences and Technology is sponsoring a conference on Advanced Automation Systems Applied to Public Services. To be held in the spring of 1974 at the Gaithersburg. Md.. site. the conference will focus on new developments in advanced automation systems and remote manipulator technology. The conference is being held to identify usee needs in these areas, to identify obstacles in the utilization of advanced automation and manipulator systems, and to recommend future action for government, industry, and labor.

For information. contact E. G. Johnsen. NBS. A130 Technology Building. Washington. D.C. 20234.

FIRE SERVICE LOCATION-ALLOCATION MODELS

How many fire houses should a city have? Where should they be located for maximum efficiency and effectiveness? Since fire services are taking increasing slices of city budgets, there is a pressing need for tools to analyze the problem and find the optimum location for the service centers. NBS Technical Note 774, Fire Service Location-Allocation Models by D. Colner and D. Gilsinn, provides a perspective on the fire-station location problem for operations researchers, mathematicians. and planners. It includes compilation of the various types of such models that analyze the impact of varying the number and location of fire stations.

NBS Technical Note 774 is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402, by SD Catalog No. C13.46:774 for 75 cents. □

U.S. GOVERNMENT PRINTING OFFICE : 1973 O - 520-505

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